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Highly selective and sensitive nanoprobes for Hg(II) ions based on photoluminescent gold nanoclusters

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ABSTRACT

We report a facile strategy to synthesize a novel fluorescent gold nanoclusters (NAC-AuNCs) in one step by using only the reactants of $HAuCl_4$ and *N*-acetyl-L-cysteine. The as-prepared AuNCs exhibited a fluorescence emission at 590 nm and a quantum yield of 13.6%. On the basis of metallophilic Hg^{2+}–Au^{+} interaction-induced fluorescence quenching mechanism, the fluorescent NAC-AuNCs offer highly sensitivity with a limit of detection of 0.2 nM for determination of Hg^{2+} ions, which is 50 times lower than the limit value (10 nM) defined by the U.S. Environmental Protection Agency in drinkable water. The proposed fluorescent probe has a linear response range of 2.0–3200 nM Hg^{2+} ions and good repeatable response to 20 nM Hg^{2+} with a relative standard deviation of 3.2% ($n = 6$). Also, the luminescence response of the NAC-AuNCs probe in the presence of EDTA is especially selective to Hg^{2+}. The proposed method has been successfully applied for determination of Hg^{2+} in various water samples, and the results agreed well with those obtained by the ICP-AES method.

1. Introduction

Contamination by various heavy metals ions, especially mercuric ions (Hg^{2+}), is of great concern, since these ions widely exist in living organisms and environments with highly toxic and bioaccumulative properties [1,2]. Some epidemic and chronic diseases have always been found because of the excess up-take of Hg^{2+} by brain, stomach and kidney [3–6]. The United States Environmental Protection Agency (US EPA) has mandated an upper limit of 2 ppb (10 nM) for Hg^{2+} in drinking water [7]. Therefore, the monitoring of Hg^{2+} level has become critically necessary in environmental and biomedical fields.

Until now, various analytical techniques such as mass spectrometry [8], atomic absorption spectrophotometry [9,10], atomic fluorescence spectrometry [11], X-ray fluorescence spectrophotometry [12] and electrochemical methods [13] have been generally applied to the detection of Hg^{2+}. However, these methods require sophisticated instrumentation and/or sample preparation, which restrict their practical applications. So far, fluorimetric assay has been proved to be an extremely powerful method to quantitative analysis because of its good reproducibility, measurement speed and high sensitivity. Thus the custom-designed of innovative fluorescent sensor for Hg^{2+} has attracted increasing attentions. Compared to the successful Hg^{2+} probes including organic dyes and semi-conductor quantum dots, gold nanomaterials are superior in chemical inertness and possess distinct inherent benefits, such as very interesting morphology-dependent chemical, electrical, biocompatibility, and optical properties that are different from their bulk counterparts. In response to the challenging task for Hg^{2+} detection, Cao et al. synthesized BSA-stabilized fluorescence gold nanoclusters (AuNCs) and realized detection for Hg^{2+} with a limit of detection (LOD) of *ca.* 8 nM [14]. Huang et al. proposed a Hg^{2+} sensing method based on gold nanoparticles (AuNPs) in the presence of aggregation agent penicillamine and the LOD toward Hg^{2+} is *ca.* 25 nM [15]. Recently comprehensive considering for exploring more sensitive methods to satisfy the Hg^{2+} detection limit that US EPA mandated is highly desirable. Cai et al. developed a method for preparation of fluorescent gold nanoclusters (AuNCs) using bovine serum albumin/poly(ethylene oxide) electrospun membrane to detect Hg^{2+} with a LOD of 57 pM [16]. Huang et al. unveiled a new assay for detection of Hg^{2+} based on 11-mercaptoundecanoic acid protected AuNPs in the presence of 2,6-pyridinedicarboxylic acid with a LOD of 5 nM [17]. Chai et al. reported a bovine serum albumin functionalized fluorescent AuNPs probe for detection of Hg^{2+} and aqueous Hg^{2+} with a LOD of 0.1 nM [18]. However, the above fluorescent AuNPs suffer from

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multiple/complex routes, or long reaction times, or the involvement of toxic/expensive reagents or extra chemical reagents. From the point of view of materials synthesis and sensing applications, it is still highly desired to develop new strategy toward rapid and green synthesis of AuNCs with a lower Hg^{2+} detection limit.

N-Acetyl-L-cysteine (NAC) is a therapeutic drug used as a mucolytic reagent, and in the treatment of acetaminophen hepatotoxicity. NAC has been used as a protected ligand to synthesize AuNPs in our previous study [19], in which $NaBH_4$ was employed as a reducing reagent according to the modified Brust-Schiffrin method. In this work, the fluorescent *N*-acetyl-L-cysteine stabilized gold nanoclusters (NAC-AuNCs) are synthesized by a one-pot approach as depicted in Scheme 1, in which NAC is the reducing-cum-protecting reagent and the reactions are green and atom-economic processes, only involving the reactants of $HAuCl_4$ and NAC. We have demonstrated that as-prepared NAC-AuNCs could be applied to Hg^{2+} detection, exhibiting high sensitivity and excellent selectivity to Hg^{2+} with a LOD as low as 0.2 nM which is 50 times lower than the maximum level permitted by the US EPA. The linear range is estimated to be 2.0–3200 nM. The feasibility of the AuNCs for analysis of Hg^{2+} in a real tap water, lake water and sewage samples has also been demonstrated successfully.

2. Materials and methods

2.1. Materials

N-Acetyl-L-cysteine (NAC) was obtained from International Laboratory (San Bruno, CA, USA). Hydrogen tetrachloroaurate trihydrate ($HAuCl_4{\cdot}3H_2O$) was provided by Aldrich (Milwaukee, WI, USA). Glacial acetic acid (CH_3COOH), absolute ethyl alcohol (CH_3OH) and metal salt as $HgCl_2$ were purchased from Tianjin Chemical Reagent Company (Tianjin, China). 10 mM phosphate buffer solutions (PBS) were prepared by mixing appropriate volumes of standard solutions of 10 mM Na_2HPO_4 and 10 mM NaH_2PO_4. Cellulose ester membrane tube (500 Da cut-off) was purchased from Spectrum Laboratories (Rancho Dominguez, CA, USA). Ultrapure water (Milli-Q) with a resistivity of 18.2 MΩ was used as the general solvent throughout the study. All reagents of analytical reagent grade or above were used as received.

2.2. Synthesis of NAC-AuNCs

NAC-AuNCs was synthesized based on a reported Au–thiolate NCs method with some minor modifications [20]. All glassware was thoroughly cleansed with *aqua regia* (HNO_3/HCl, 1:3) and rinsed extensively with Milli-Q water prior to use. Freshly prepared solutions of $HAuCl_4$ (0.10 M, 0.40 mL) and NAC (0.10 M, 0.60 mL) were mixed in 1.6 mL MeOH/glacial acetic acid (6:1, v/v) solution under magnetic stirring at 25 °C for 30 min. 8.7 mL Milli-Q water was then added to the mixture; subsequently, the solution was heated to 70 °C with reflux under magnetic stirring for 24 h. NAC-AuNCs with strong orange fluorescence was obtained. A cellulose ester dialysis membrane (MWCO 500 Da) was then used to separate NAC-AuNCs from any residual unreacted species and side products. After dialysis for 3 days, the solvent (H_2O) was removed by a freeze-dryer. And the solid NAC-AuNCs products were obtained.

2.3. Instrumentation

UV–vis absorption spectrum was recorded on a Shimadzu UV-2450 absorption spectrophotometer (Tokyo, Japan). Fluorescence intensities and lifetimes were measured using an Edinburgh Instrument FLS-920 time-resolved/steady state fluorescence spectrometer (Livingston, UK). pH measurements were taken on a FE20 pH-meter (Mettler Toledo Instrument Inc, Shanghai, China). Transmission electron microscopic (TEM) images were obtained on a JEOL JEM-2100 (Tokyo, Japan) at an accelerating voltage of 200 kV. X-ray photoelectron spectrum (XPS) was acquired on a Leybold Heraeus SKL-12 X-ray photoelectron spectrometer (Shenyang, China). Fourier transform infrared (FTIR) spectra were captured on a PerkinElmer Paragon 1000 FTIR spectrometer (Waltham, MA, USA). The zeta potential was performed with a Malvern Instruments Nano-ZS90 Zetasizer (Malvern, UK). ICP-AES measurement was carried out on a Thermo iCAP 6300 atomic emission spectrometer.

2.4. Detection of Hg^{2+}

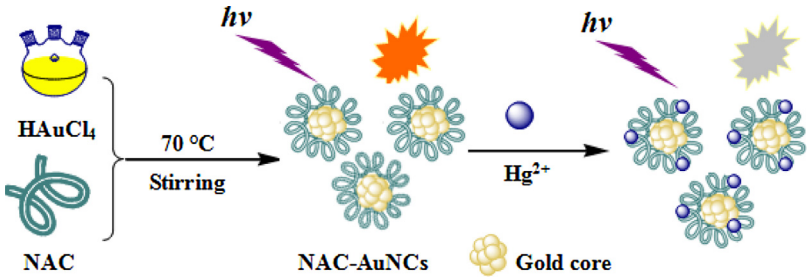
An aliquot of NAC-AuNCs was added to 5.0 mL PBS (10 mM, pH 8.0) containing various concentrations of Hg^{2+}. The solution was mixed thoroughly on a vortex mixer and incubated for 10 min at room temperature. The fluorescence spectra were then recorded (excitation 340 nm and peak emission 590 nm). The slit widths for the excitation and emission were both set at 3.0 nm. The interfering effects of other ions were investigated individually in the presence of NAC-AuNCs.

Tap water, lake water and sewage samples were collected from our laboratory, Ling De Lake on the campus of Shanxi University and Sewer Ditch at Taiyuan, respectively. All the raw samples were centrifuged (13,000 rpm) and filtered through a 0.45-μm cellulose membrane to remove any suspended particles. A series of samples was prepared by spiking standard solutions (0.50 mL) containing various concentrations of Hg^{2+} in 10 mM PBS (pH 8.0) into the real samples (0.50 mL). The resulting solutions were further mixed with NAC-AuNCs solutions. After a 10-min incubation period, the fluorescence spectra were recorded (excitation wavelength 340 nm).

3. Results and discussion

3.1. Characterization of NAC-AuNCs

Fig. 1A depicts the TEM image of the NAC-AuNCs, showing that the diameters of the NCs are 1–2 nm. The FTIR spectra of the pure



Scheme 1. Schematic sketch for synthesis of fluorescent NAC-AuNCs and the application in the detection of Hg(II). It did not represent accurate quantitative relation between NAC-AuNCs and Hg(II).